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(54) LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a positive electrode active material for safe battery, having a long lifetime and a high capacity by adding at least one or more kinds of elements except for Li, Mn and oxygen to the oxide having a specified spinel type structure at a mole ratio in a specified range with respect to the total quantity of Mn.

SOLUTION: This positive electrode active material is an oxide, having the spinel type structure represented by a formula Li1+xMn2-xO4 (0<x<1.33). At least one or more kinds of elements except for Li, Mn and oxygen is added at 0.01-10% of mole ratio with respect to the total amount of Mn. At least one element from among B, P, Mg, As, Sb, Zr, Na, Be, Y, Si, Al, C, F, Bi,Pb, Ge, Sn is preferably added at 0.01-10% in mole ratio. One or more kinds of elements except for Li, Mn, oxygen transition metal M is preferably added to the oxide having a spinel structure represented by a formula Li1+xMyMn2-x-yO4 (0<x<1.33, 0<y<2, M is at least one or more kinds of transition metals which differs from Mn) at 0.01-10% of mole ratio with respect to the total amount of Mn.

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CLAIMS

[Claim(s)]
[Claim 1] It is an active material for producing the rechargeable battery in which charge and discharge are possible, when a lithium ion carries out insertion. An oxide with the spinel type structure specified with a chemical formula is received at the total amount of Mn in at least one or more kinds of elements other than Li, Mn, and oxygen. Li1+xMn2-xO4 (0< x<1.33) -- a mole ratio -- 0.01% from -- lithium rechargeable battery using the active material ingredient characterized by adding to 10%, and this matter as a positive-electrode ingredient.
[Claim 2] It is an active material for producing the rechargeable battery in which charge and discharge are possible, when a lithium ion carries out insertion. An oxide with the spinel type structure specified with a chemical formula is received at the total amount of Mn. Li1+xMn2-xO4 (0< x<1.33) -- a mole ratio -- 0.01% from -- lithium rechargeable battery using the active material ingredient characterized by adding at least one element to 10% among B, P, Mg, As, Sb, Zr, Na, Be, Y, Si, aluminum, C, F, Bi, Pb, germanium, and Sn, and this matter as a positive-electrode ingredient.
[Claim 3] It is an active material for producing the rechargeable battery in which charge and discharge are possible, when a lithium ion carries out insertion. An oxide with the spinel type structure specified with a chemical formula is received at the total amount of Mn in at least one or more kinds of elements other than Li, Mn, and oxygen. Li1+xMn2-xO4 (0< x<1.33) -- a mole ratio -- 0.01% from -- the active material ingredient for rechargeable batteries characterized by adding to 10%, heat-treating and being obtained from 400 degrees C at the temperature of 900 degrees C, and its manufacture approach.
[Claim 4] It is an active material for producing the rechargeable battery in which charge and discharge are possible, when a lithium ion carries out insertion. Li1+xMyMn2-x-yO4 (at least one or more kinds of different transition metals from 0< x<1.33, 0< y<2, and M:Mn) -- to an oxide with the spinel type structure specified with a chemical formula at least one or more kinds of elements other than Above Li and Mn, oxygen, and the transition-metals element M -- the total amount of Mn -- receiving -- a mole ratio -- 0.01% from -- lithium rechargeable battery using the active material for rechargeable batteries and this which are characterized by being added and obtained to 10%.
[Claim 5] The lithium rechargeable battery using the active material for rechargeable batteries and this which are characterized by at least one alloying element from which Above Li and the **** metallic element M differ being at least one of B, P, Mg, As, Sb, Zr, Na, Be, Y, Si, aluminum, C, F, Bi, Pb, germanium, and Sn in above-mentioned claim 4.
[Claim 6] It is an active material for producing the rechargeable battery in which charge and discharge are possible, when a lithium ion carries out insertion. It is an oxide with the spinel type structure specified with a chemical formula. Li1+xMyMn2-x-y-zBzO4 (at least one or more kinds of different transition metals from 0< x<1.33, 0<y+z<2, and M:Mn) -- For Li, Mn, oxygen, and transition metals M, the element B which permutes Mn is a lithium rechargeable battery using the active material for rechargeable batteries and this which are characterized by being at least one or more kinds of different elements.
[Claim 7] The lithium rechargeable battery using the active material for rechargeable batteries and this which are characterized by adding at least one or more kinds of elements other than Li, Mn, oxygen, the transition-metals element M, and the permutation element B from 0.01% to 10% to the total amount of Mn at the active material ingredient of above-mentioned claim 6, and being obtained by the mole ratio.
[Claim 8] When a lithium ion carries out insertion, it is an active material for producing the rechargeable battery in which charge and discharge are possible, and is 1(Li, A)+xMyMn2-x-y-zBzO4 (0< x<1.33, 0<y+z<2, at least one or more kinds of different transition metals from M:Mn, at least one or more kinds of different elements from A:Li.). (Li, A) mean that both Li and the element A are included. For Li, Mn, and transition metals M, the element

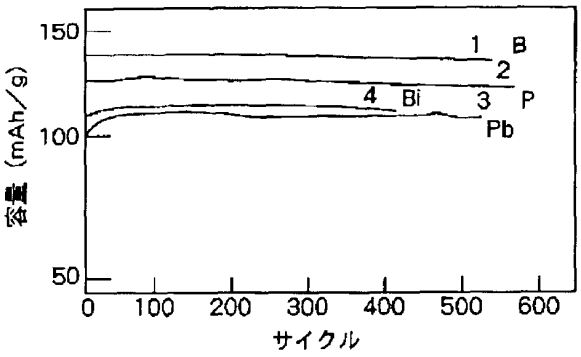
B'which is an oxide with the spinel type structure specified with a chemical formula, and permutes Mn is a lithium rechargeable battery using the active material for rechargeable batteries and this which are at least one or more kinds of different elements, and are characterized by the permutation elements A being Mg, Zn, Fe, Cu, and nickel.

[Claim 9] at least one element which is different into the active material ingredient of above-mentioned claim 6 in Li, Mn, oxygen, the transition-metals element M, and the permutation elements A and B -- the total amount of Mn -- receiving -- a mole ratio -- 0.01% from -- lithium rechargeable battery using the active material for rechargeable batteries and this which are characterized by being added and obtained to 10%.
[Claim 10] The lithium rechargeable battery using the active material for rechargeable batteries and this which are the spinel mold oxide specified by above-mentioned claims 1-9 for producing the rechargeable battery in which charge and discharge are possible when a lithium ion carries out insertion, and are characterized by a lattice constant being more greatly [than 8.10A] smaller than 8.25A.
[Claim 11] The portable information communication equipment characterized by using the lithium rechargeable battery using the active material for rechargeable batteries of a publication for above-mentioned claims 1-9 as a power source, portable video, personal computer consumer electronics, the stationary-energy-storage system for power, and an electric vehicle.

[Translation done.]

Drawing selection Representative drawing

図 1



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the active material for lithium rechargeable batteries and lithium ion rechargeable battery which used nonaqueous electrolyte.
[0002]
[Description of the Prior Art] Although it is expected that the spread of a personal computer, cellular phones, etc. will increase increasingly with development of an information society from now on, in connection with this, the formation of a high energy consistency of the cell which is the power source of a portable equipment, and high capacity-ization are demanded increasingly. Since cell voltage is a high energy consistency highly, development is prosperous in the lithium rechargeable battery using nonaqueous electrolyte, and it also has a part of cell put in practical use. However, it is in charge of utilization and there is a trouble of shoes in Mn system spinel ingredient used as current and a positive-electrode ingredient.
[0003] The first, it is degradation of a cycle life first. Since, as for the spinel mold oxide, trivalent manganese ion has yarn teller instability, if charge and discharge are repeated, the capacity will deteriorate remarkably. Moreover, it is the problem of elution which Mn begins to melt into the second into the electrolytic solution, and brings about degradation of the engine performance. It is the problem of safety that a positive electrode causes generation of heat and ignition in the third in the case of a short circuit or collapse.
[0004] Each of these is troubles whose solution is possible by increasing the structural stability of positive active material. With the conventional positive-electrode ingredient, although it was difficult to solve these, some attempts are already reported.
[0005] According to JP,6-187933,A by the technology finance company, improvement in a cycle life and prevention of elution are aimed at by using spinel mold oxide Li1+xMn2-xO4 (0<=x<1.33) which changed the presentation ratio of Li and Mn as an active material. Moreover, the same thing is tried by permuting by Co instead of Mn. However, there is a trouble of reducing the initial capacity itself, by such approach.
[0006] Moreover, if based on a open patent (Taira 9-147867 number) of MORIENAJI Li1+xMzMn2-x-zO4 (transition-metals elements, such as 0<=x<0.33, M:Co, and Cr, --) which permuted Mn by transition-metals elements, such as Co and Cr, further in the spinel mold oxide which made the presentation ratio to Mn of Li high Although improvement in a cycle-life property is aimed at by using as positive active material, the life of 1000 or more cycles needed for utilization is not acquired.
[0007]
[Problem(s) to be Solved by the Invention] As mentioned above, the crystal structure of a positive-electrode ingredient is stabilized by more various approaches than before, and the reinforcement of a cell, elution prevention, improvement in safety, etc. are tried. However, when cell capacity fell when reinforcement was attained, and high capacity-ization was attained contrary to this, a problem was produced at safety and an internal short circuit took place, there was a trouble that generation of heat and ignition occurred. The spinel mold oxide positive-active-material ingredient and its manufacture approach for this invention supplying a safe high capacity cell long lasting are offered.
[0008]
[Means for Solving the Problem] in order to attain the technical problem of this invention -- Li1+xMn2-xO4 (0< x<1.33) -- the positive-electrode ingredient which added at least one or more kinds of elements other than Li, Mn, and oxygen is used for an oxide with the spinel type structure specified with a chemical formula. If the presentation ratio of Li and Mn will be called a Li/Mn ratio, raising the above-mentioned Li/Mn ratio will act so

that a lattice constant may be made small, and, for this reason, the crystal structure will be stabilized.

[0009] This acts so that improvement in a cycle property and elution may be prevented, and it brings about the effectiveness of improvement in a battery life property. However, raising a Li/Mn ratio will bring about the fall of geometric capacity, and it is not avoided that an actual initial capacity also falls. In an actual cell, the capacity of a cell will be prescribed by the capacity of a positive-electrode ingredient, and the capacity fall of a positive-electrode ingredient is not desirable.

[0010] In this invention, the ingredient which added at least one or more kinds of elements other than Li, Mn, and oxygen is used for the spinel mold Mn oxide positive-electrode ingredient specified by the above-mentioned empirical formula Li1+xMn2-xO4 ($0< x<1.33$). As an element to add, it is desirable to add at least one element among B, P, Mg, As, Sb, Zr, Na, Be, Y, Si, aluminum, C, F, Bi, Pb, germanium, and Sn. the total amount of Mn which contains the addition into a positive-electrode ingredient -- receiving -- a mole ratio -- 0.01% from -- although even 10% is desirable, it is also added more than this, and it is satisfactory even if it is the following amounts.

[0011] Especially addition of B, P, and Sb can be high-capacity-ized, without changing the crystal structure (i.e., without it maintaining stability and spoiling a life property). Moreover, from the point of raising safety, the permutation of aluminum, Si, Ga, and Mg is effective. It is most suitable to be referred to as $0.02< x<0.14$ as a presentation ratio of the ingredient for adding in the empirical formula which becomes Li1+xMn2-xO4.

[0012] Moreover, it is a thing making it be the following for manufacturing the positive-electrode ingredient by this invention. First, Mn system spinel mold oxide used as the charge of a base material is produced. For that, as a manganese raw material, MnO2 (it does not matter even if it is the manganese dioxide (CMD) chemically refined even if it was electrolytic manganese dioxide (EMD).), Mn 3O4, Mn2O3, MnO and MnCO3, MnCOOH, MnOOH, etc. are used, using Li2CO3, LiOH, LiNO3, LiCOOH, Li2O, etc. as a lithium raw material.

[0013] What carried out precipitate desiccation after mixing these by the predetermined presentation ratio or mixing in a solution is used as a raw material. A raw material is calcinated in air or an oxygen air current for 40 hours. Although the burning temperature at this time is based also on a presentation ratio, its range which is about 600 degrees C - 900 degrees C is desirable. This is behind heat-treated in the charge of a base material which was able to obtain the predetermined daily dose to add an additive. The temperature of heat treatment has the desirable temperature of 400 to 900 degrees C. Of course, although there is effectiveness of addition of not heat-treating, either, ****** heat-treats more.

[0014] Moreover, in order to solve this technical problem, the following positive-electrode ingredients are used. the above-mentioned active material -- Li1+xMyMn2-x-yO4 (at least one or more kinds of different transition metals from $0< x<1.33$, $0< y<2$, and M:Mn) -- at least one or more kinds of elements other than Above Li and Mn, oxygen, and the transition-metals element M are added to an oxide with the spinel type structure specified with a chemical formula, and it is obtained. As an element to add, it is desirable that it is at least one of B, P, Mg, As, Sb, Zr, Na, Be, Y, Si, aluminum, C, F, Bi, Pb, germanium, and Sn.

[0015] It is an oxide with the spinel type structure specified with a chemical formula. moreover -- in order to solve a technical problem -- Li1+xMyMn2-x-y-zO4 (at least one or more kinds of different transition metals from $0< x<1.33$, $0<y+z<2$, and M:Mn) -- For Li, Mn, oxygen, and transition metals M, the element B which permutes Mn is a lithium rechargeable battery using the active material for rechargeable batteries and this which are characterized by being at least one or more kinds of different elements. As B, the **** metallic element M may have a different transition-metals element, for example, Sc, Ti, V, Cr, Mn, Fe, Co, nickel, and Cu, or desirable Zn, and typical elements aluminum, Ga, In, Sn, and Pb etc. are sufficient. Moreover, alkalinity metals, such as Mg, Sr, and calcium, are sufficient.

[0016] Moreover, in this invention, in order to solve a technical problem, at least one or more kinds of elements other than Li, Mn, oxygen, the transition-metals element M, and the permutation element B are further added by making the above-mentioned positive-electrode ingredient into the charge of a base material. As an element to add, it is desirable that it is at least one of B, P, Mg, As, Sb, Zr, Na, Be, Y, Si, aluminum, C, F, Bi, Pb, germanium, and Sn. In order to use as a positive-electrode ingredient, after adding, it is desirable to heat-treat at the temperature for 400 degrees C to 900 degrees C.

[0017] in order [moreover,] to solve this technical problem -- 1(Li, A)+xMyMn2-x-y-zBzO4 ($0< x<1.33$, $0<y+z<2$, at least one or more kinds of different transition metals from M:Mn, at least one or more kinds of different elements from A:Li.) -- positive active material with the spinel type structure specified with a chemical formula is used. Here, (Li, A) mean that both Li and the element A are included. Li, Mn, and transition metals M are at least one or more kinds of elements with which the elements B which permute Mn differ, and its permutation

element A is [that they are Mg Zn, Fe, Cu, and nickel] desirable. Moreover, other elements can be added to the above-mentioned active material, and it can also consider as a positive-electrode ingredient.

[0018] Moreover, in order to solve a technical problem, the lattice constant of these spinels mold oxide is larger than 8.10A, and it is 8.25. It is made to become smaller than angstrom. Thus, an improvement of a cycle property is achieved by selecting the matter with a small lattice constant as a positive-electrode ingredient. This can be attained selecting an element with a small ionic radius as a permutation element as the means, and by making the cooling rate after calcinating as late as possible. As for a cooling rate, it is desirable that it is [3 degree-C] the following by /. Moreover, calcinating in an oxygen air current also has the same effectiveness.

[0019] Using the positive active material by this invention, for forming a rechargeable battery positive electrode, it is based on the following approaches. First, positive active material is kneaded with the carbon as electric conduction material. Subsequently, a resin binder is added to this as a binder, after kneading further, it applies on an electrode base, and press desiccation is carried out. As a negative electrode, amorphous system carbon material, graphite system carbon material, etc. are suitable.

[0020] These negative-electrode ingredients are not affected at all at the purpose of invention, even if it is electrode active materials other than ****. For example, a stannic-acid ghost etc. can be used. Moreover, electrolytes, such as a solid electrolyte which has the conductivity of the organic electrolytic solution made to dissolve the lithium salt chosen from LiClO4, LiAsF6, LiBF4, and LiPF6 grade as quality of an electrode in non-aqueous solvents, such as propylene carbonate, a propylene carbonate derivative, and ethylene carbonate, for example or a lithium ion, or a gel electrolyte, can be used.

[0021] Moreover, even if it uses a microporous separator according to the need on the configuration of a cell, the effectiveness of this invention is not spoiled at all. The positive electrode, negative electrode, and separator which were produced are rolled round considering a center pin as an alignment, are inserted into tubed or the container of a square shape, pour the electrolytic solution into after an appropriate time, and are sealed.

[0022] Especially the application of the cell of this invention is not limited. Although the application indicated by claim 11 is typical In addition to this for example, a notebook computer, a pen input personal computer, a pocket personal computer, a note type word processor, a pocket word processor, an Electronic Book player, a cellular phone, and a cordless phon -- a cordless handset, a pager, a handy terminal, a pocket copy, an electronic notebook, a calculator, a liquid crystal television, and an electric shaver -- A power tool, an electronic translating machine, a land mobile radiotelephone, a transceiver, an utterance input machine, memory card, a backup power supply, a tape recorder, radio, a headphone stereo cassette tape recorder, a pocket printer, a handicap cleaner, portable CD, a video movie, The power source for devices, such as a navigation system, It can be used as a power source of a refrigerator, an air-conditioner, television, a stereo, a calorifier, an oven microwave oven, a tableware washing machine, a washing machine, a drier, a game device, a lighting device, a toy, a load conditioner, medical equipment, an electric vehicle, a golf cart, an electric cart, etc. Moreover, it is usable to the system for large-sized stationary energy storage, the object for munitions, and the object for space besides these noncommercial uses.

[0023] That is, it acts as a positive-active-material ingredient.

[0024]

[Embodiment of the Invention] An example is given to below and this invention is explained. In addition, this invention is not limited to the example described below.

[0025] (Example 1) Li1+xMn2-xO4 which is a charge of a base material first It produced. The production approach is as follows. First, electrolytic manganese dioxide (EMD) is mixed with a lithium carbonate by the predetermined mole ratio. Then, it calcinates from 10 hours at the temperature between 900 degrees C from burning temperature 650 for about 40 hours. An ambient atmosphere performs this in air or an oxygen air current. The alloying element was added to the obtained charge of a base material (this example x= 0.08). A boric acid, phosphate, and other oxides are used as a raw material for adding an alloying element. The percentage of addition is 0.25% to the number of mols of Mn in an active material ingredient. It was made to become.

[0026] The mixed charge of a base material and the charge of add-in material heat-treated in 10-hour air at the temperature of 300 to 600 degrees C. At this example, it classified with the screen of 45 microns of diameters of a mesh, and it kneaded with a binder and electric conduction material, applied on aluminum foil, and considered as the positive electrode by drying after a press. LiPF6 The charge and discharge test was performed using the nonaqueous electrolyte to contain. Initial capacity, the capacity maintenance factor after 100 cycles, and the effectiveness of an alloying element are shown in Table 1.

[0027]

[Table 1]

表 1

添加元素	初期容量 (mAh/g)	容量維持率 (%)	添加の効果
無し	107	98	
B	125	97.5	容量の増加。
P	128	98.2	容量の増加。
Al	105	99.5	サイクル特性の向上。溶出量低減。発熱抑制。
Si	102	99.3	発熱量抑制。
Mg	105	99.7	サイクル特性向上。溶出量低減。

[0028] It turns out that these alloying elements act so that the crystal structure may be stable, and effectiveness is in improvement in a cycle property, and control of elution and the improvement in safety which prevents exoergic ignition by this.

[0029] (Example 2) The example of another this invention is shown below again. As a charge of a base material, Li1+xCoyMn2-x-y-zMgzO4 (x= 0.10, y= 0.10, z= 0.15) was produced. B, Sn, Bi, and Pb were further added to this. The heat treatment temperature after addition performed heat treatment of 10 hours as 400 degrees C. A cycle property is shown in drawing 1 . In any [these] case, improvement in capacity is found. Moreover, degradation of a cycle property is not seen compared with an additive-free ingredient.

[0030] (Example 3) The result of having investigated the rate dependency of a discharge property is further shown in drawing 2 by using the positive-electrode ingredient by this invention as an active material. The case where an additive-free positive-electrode ingredient is used as an example of a comparison is shown. The empirical formula of an additive-free ingredient is Li1+xMn2-xO4 (x= 0.08). With an additive-free spinel mold positive-electrode ingredient, it is a discharge rate (however, it means that 1C charges in 1 hour.). 2C is 0.5 to a full charge. It is the semantics of time amount. Although capacity is seen deteriorate as it becomes high, with the ingredient which added Sn and In, it turns out that there is little degradation of capacity. Preventing raising the electronic conduction nature of a positive-active-material ingredient, and the particle of an active material carrying out the charge up to high-speed charge and discharge by this has an operation of these additives.

[0031]

[Effect of the Invention] High capacity and the long lasting active material for rechargeable batteries are obtained by this invention, and offer of high capacity applicable to a pocket device or an electric vehicle by this, high insurance, a long lasting cell, and a group cell is attained.

[Translation done.]